

# PATENT SPECIFICATION

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## (54) PROCESS FOR IMPROVED MAGNETIC BENEFICIATION OF CLAYS

(71) We, J. M. HUBER CORPORATION, a Corporation of the State of New Jersey, U.S.A. located at Locust, State of New Jersey, U.S.A., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to processes for improving the brightness of clays, such as the kaolin clays utilized in the manufacture of paper, and more specifically relates to a process for improving the magnetic beneficiation of said clays.

Naturally occurring kaolin clay deposits are known to contain discoloring contaminants. Commonly, for example, iron and titanium minerals, as well as other minerals such as montmorillonite and mica, may in various combinations be responsible for such discoloration. The titanium minerals, for example, are commonly present as TiO<sub>2</sub> (e.g. in the form of anatase), and such minerals vary from yellow to dark brown in color. Similarly, in the case of montmorillonite, such mineral is known to be magnetic and to have the ability to capture staining surface iron because of its high cation exchange capacity. These various cited impurities are largely responsible for the yellow-brown shade of many kaolins. Indeed the clay is often rejected as being unsuitable for commercial use, solely on the basis of color, even though its other physical properties, such as the viscosity of clay-water slurries and particle size distribution are within desired limits.

The brightness of clay usually is increased during processing by fractionation: the finer the particle size the brighter the clay. However, this increase is usually insufficient for the more discolored clays to be rendered acceptable commercially, and additional treatment is required of the fine clay, such as chemical leaching. Leaching with chemicals such as

zinc or sodium hydrosulphite thus generally results in improving brightness of the refined clay slurries, although an increase of only 2 to 5 brightness points is usually obtained. There are other known methods of improving brightness of clays, but generally these techniques are quite expensive and do not give sufficient increase in brightness to justify the cost.

In the past numerous attempts have been made to remove contaminants by the use of magnetic techniques, where the said contaminants are responsive to magnetic attraction. Such techniques utilize the force of a magnetic field gradient to cause differential movement of mineral grains through the said field. In U.S. Patent No. 3,471,011, for example, magnetic beneficiation of kaolin clay is taught utilizing techniques wherein a slurry of clay in water is subjected to a high intensity magnetic field of at least 8,500 gauss, with the time of retention in the field being from 30 seconds to 8 minutes — in order to separate particles of low magnetic susceptibility from the slurry. More recently in British Patent No. 1,347,396, apparatus and methodology are taught wherein a clay-water slurry is passed through a canister packed with steel wool or similar highly irregular and porous ferromagnetic material. In the presence of an intense magnetic field, the combination set forth has been found to be highly effective in moving the magnetically attractable contaminants, by virtue of the ability of the said system to concentrate the field at myriad points in the canister volume at which attraction may occur.

While magnetic separation techniques such as those set forth above, have therefore been found to be of great value in removing certain contaminants from the clay slurries, and indeed result in several points increase of brightness in the treated products, it is nevertheless found in practice that various of the contaminants are removed only with the greatest difficulty. Among other things, it may be

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noted that the factor of retention time in the magnetic field has been found to be of great importance in removing certain of these relatively intractable contaminants, with removal being greatly augmented as retention times increase. Unfortunately, however, this factor of retention time is one which must be traded off against the economics of a processing situation. This is to say, that the use of long retention period (and sometimes multiple-pass processing) results in inefficient employment of the large scale and expensive magnetic separating machinery as the slurry passes through the said separator — with consequent losses elsewhere on the production line. Accordingly, it is of considerable interest to discover those techniques which may improve the magnetic separation methodology, both with respect to removal of contaminants previously deemed incapable of treatment; and as well to expediting removal of these contaminants which were known to be magnetically removable, but have in the past required unacceptable retention periods in the magnetic field to accomplish same.

In the foregoing connection it may be noted that in U.S. Patent No. 3,371,988, it has been disclosed that contrary to the practices of the prior art, wherein clay slurries prior to classification are treated with a peptizing agent in order to achieve minimum viscosity (that is to say, maximum dispersion of clay particles to facilitate fractionation), the reflocculated state has unexpected utility because it apparent creates a system for the controlled release of titanium contaminants. It is thus taught in said patent that fractionation in the reflocculated state is capable of achieving preferential separation of the said titanium impurities, resulting in a significant increase in purity and brightness of the refined kaolin fraction. These differential flocculation techniques, however, relying as they do on differential sedimentation, change the particle size distribution in the slurry, and provide relatively low yields. It has not been conceived that the findings of U.S. Patent 3,371,988 could bear upon magnetic separation techniques, in that (among other things) it has been consistently believed that magnetic separation should properly be performed at minimum viscosity of the slurry being treated. Furthermore, since magnetic separation is usually accomplished at slurry concentrations of about 30% solids, the presence of chemical agents which would place a high solids content slurry in a reflocculated state would not substantially affect the viscosity of the low solids content slurry.

In accordance with the foregoing, it may be regarded as an object of the present invention, to provide an improved process for magnetically removing discoloring contaminants from clay-water slurries, which process enables highly efficient removal of said contaminants.

It is a further object of the present invention to provide an improved process for magnetically removing discoloring contaminants from clay-water slurries, which enables removal of said contaminants with increased rapidity, and elimination of multiple-pass processing, whereby to render practical high rate and large scale treatment of the said slurries.

It is another object of the present invention, to provide an improved process for magnetically removing discoloring contaminants from clay-water slurries, wherein the efficiency of the process is so improved that it is not essential to utilize magnetically saturated matrices.

It is still a further object of the present invention, to provide a process for removing discoloring contaminants from clay-water slurries, which is effective with even relatively high solids-content slurries, and which does not introduce fractionation, low yield, or substantial change in particle size distribution characteristics.

According to the present invention, there is provided a method for removing discolorants from a clay comprising the steps of adding an oxidant to an aqueous slurry of a clay having weakly magnetically susceptible contaminant particles in minor concentration bound to the surface of the clay, so as to release chemically said particles from the clay surface, and magnetically separating the thus released particles from the clay.

The oxidant is preferably sodium hypochlorite which may be added in an amount of from 1/2 to 4 pounds/ton of clay or up to 2 pounds/ton of clay.

Alternatively, the hypochlorite may be added in an amount of from 1/2 to 8 pounds/ton of clay in said slurry, and further including the step of adding to the aqueous slurry one or more dispersing agents to reduce the viscosity of said aqueous slurry.

The dispersing agent(s) may be sodium metasilicate and/or sodium hexametaphosphate. Each of these compounds serves to effect a viscosity reduction in the clay slurry. The sodium hexametaphosphate also assists the releasing process.

Preferably, up to 2 pounds and most preferably 1 to 2 pounds per ton clay of said sodium hexametaphosphate, and between 4 and 15 pounds per ton clay of said sodium metasilicate in the anhydrous form are

added to the slurry and the pH in said slurry is maintained in the range of from 7 to 12.

Preferably, said dispersing agent(s) is or are added in concentration(s) maintaining the viscosity of said slurry below 15 centipoise.

In the drawings appended hereto:

Figure 1 is a graphical depiction, showing the effects of an oxidant and dispersants upon brightness and production rate for a representative clay thereupon subjected to magnetic separation,

Figure 2 is a graph, depicting the effects upon leached brightness, of variations in the oxidant concentration, in the treatment of a clay then subjected to magnetic separation;

Figure 3 is a graph, depicting the manner in which addition of sodium hexametaphosphate reduces the viscosity problem associated with use of sodium hypochlorite, thereby enabling magnetic separation at relatively high solids content;

Figure 4 is a graph, showing the effect of sodium hexametaphosphate addition upon leached brightness level, for various concentrations of hypochlorite; and

Figure 5 is a graph, depicting the effects upon production rate, for a representative clay subjected to magnetic separation, where such clay is subjected to treatment in accordance with the invention.

The magnetic separation techniques utilized herein, including the apparatus which may be used for such purposes, do not *per se* comprise the present invention; and accordingly such techniques and apparatus are not disclosed in detail herein. Reference may be had in this connection to British Patent No. 1,347,396, referred to above, for an example of typical apparatus which may be utilized for the present purposes. Apparatus which may be similarly employed, are also shown elsewhere, as for example, in U.S. Patent No. 3,627,678. In the aforementioned British Patent No. 1,347,396 apparatus, a magnetic field is maintained in the steel-wool matrix between pole members, at a mean intensity of at least 7,000 gauss — and preferably at considerably higher strengths (from 10,000 to 20,000 gauss) — throughout the matrix in which separation is effected. Comparable magnetic intensities may be utilized in accordance with the present techniques; however, lower fields and/or comparatively reduced retention periods in the fields may also be beneficially employed by virtue of the facility lent to magnetic separation by the presently disclosed processes.

#### Example I

In order to illustrate the effect of the agents of the invention upon the brightness

of clays subjected to magnetic beneficiation, a sample of unleached slurry of the middle Georgia type (No. 2 fraction) — i.e. with particle distribution size such that 80% by weight have an E.S.D. of less than 2 micron, containing 30% solids, was obtained from normal plant production. The clay sample was subjected to a magnetic separation treatment in apparatus of the type discussed above for a total period of 3.8 minutes. The resultant product was leached in normal fashion, and it was thereupon found to exhibit a leached brightness of 90.0 on the conventional TAPPI scale. A similar sample of the said slurry was then subjected to treatment in accordance with the invention by addition to the slurry sample of 10 pounds/ton of sodium hexametaphosphate (Calgon\* Registered Trade Mark), 6 pounds/ton sodium metasilicate (anhydrous), and 5.4 pounds/ton of sodium hypochlorite. The leached brightness of the resultant product was 91.8 on the same TAPPI scale. It will be evident from the foregoing that the clay which is treated with oxidant and dispersing agents prior to magnetic treatment, responds much better to such magnetic treatment than an untreated sample.

The full implications of the effects of the treatment upon brightness and production rate will be better appreciated by referring to Figure 1 herein, where leached brightness for clay samples as in Example I are shown versus retention time in the magnetic separator. The lower curve in Figure 1 corresponds to a "normally" dispersed clay of the type specified in the present Example, while the uppermost curve is for clay subjected to oxidant and dispersing agents as described herein, prior to magnetic separation. The said curves are of particular interest, it will be observed, in plotting the leached brightness as an ordinate against the retention time as abscissa. By examining the curves of Figure 1, it will be evident that by utilizing a combination of dispersion and oxidation treatment, the production rate of the clays can be markedly increased. In particular it is found that a 90 TAPPI brightness No. 2 clay, can in accordance with the invention, be produced at about three times the rate when processed with use of oxidants and dispersants as indicated.

The process of the present invention basically utilizes an oxidant to "free" the contaminants, as for example anatase, from the host particles, i.e. the clay. The preferred oxidant as illustrated in the foregoing Examples, comprise an oxidant such as sodium hypochlorite. The precise manner in which this agent achieves its beneficial effects is not completely understood, although it is hypothesized that

the oxidizing character of the said agent may act to break the organic bonds tending to restrain the contaminants. Similarly it is hypothesized that the said agent, i.e. the hypochlorite, promotes attainment of an isoelectric state for the contaminants. Such state, wherein a particular particle would possess no net electric charge, is important to subsequent magnetic separation in that, where achieved, large magnetic flocs can form — and the larger the impurity particle the easier is its removal by magnetic means. Similarly, the isoelectric state, where achieved, implies the absence of mutual repulsive forces among contaminant particles — which forces would have to be overcome before magnetic collection could be effective.

As will shortly be discussed, the above-mentioned oxidant can be utilized alone with effective results. However, as will also become further apparent hereinbelow, the sodium metasilicate and sodium hexametaphosphate serve important functions in the formulations set forth. In particular it is found that these added dispersants, particularly Calgon\*, permit the use of beneficially higher levels of hypochlorite than would otherwise be possible, in that the viscosity of the slurry begins to rise with NaOCl addition to a point (over about 15 centipoise) where magnetic separation is impaired. The Calgon\* is particularly effective specifically on the clay component, thereby increasing the fluidity of the host species so as to enable free migration of contaminant particules during subsequent magnetic treatment. In addition to the sodium hexametaphosphate set forth in the Examples, various silicates, tetrasodium pyrophosphate (TSPP), sodium tripolyphosphate (STPP) and other well-known dispersing agents are suitable for the present application.

The sodium metasilicate appears to act not only as a dispersing agent, but perhaps more importantly assists in placing the contaminants in the above-mentioned isoelectric state, by raising the pH of the system to a preferable level of 7 to 12. Due to this mechanism, or perhaps others not understood, the metasilicate, moreover, appears to assist or augment the release of the said contaminants from the clay. Up to 15 lbs. per ton of the said metasilicate (in the anhydrous form) are usefully employed for these purposes with 4 to 15 lbs. per ton being a preferable level of addition.

It may also be noted in the foregoing connection, that while anatase does appear to be a major component the magnetic removal of which is facilitated by the processes of the invention, it has been observed that large brightness improvements are at times achieved, with no discernible reduction in anatase. Among the explanations hypothesized for this phenomenon is that chelating organics are oxidized, which could trap multiple discolorant systems. It is also speculated that selected release and dispersion of micaceous and vermiculitic, as well as titaniferous minerals may be occurring.

#### Example II

The advantages of utilizing oxidants alone, as opposed to using such agents with additional dispersants prior to magnetic separation, are highly significant from an economic viewpoint. Aside from the need for additional materials, the use of excess dispersants may require multiple filtrations for viscosity control. Based on current costs, for example, and assuming that only oxidation is employed — by addition of the order of 2 pounds per ton of sodium hypochlorite prior to magnetic separation — the additional cost per ton under representative processing conditions is of the order of 34 cents; whereas where oxidation and excess dispersants are employed the additional costs are presently estimated to be of the order of \$2.50/ton, a relatively enormous differential. In order, therefore, to demonstrate fully the beneficial effects of utilizing oxidants alone, a study was made of the effects of sodium hypochlorite upon the leached brightness of clay samples treated with hypochlorite prior to magnetic separation and leaching (pre-magnetic-oxidation). The beneficial effects upon brightness are shown in Table I for samples of the No. 2 clay fraction referred to in Example I above, where "normal" treatment (that is, magnetic separation alone) is utilized in comparison to pre-magnetic-oxidation — utilizing in each instance 2 pounds/ton of sodium hypochlorite. As a control, data are also set forth indicating the changes in brightness achieved where samples are treated with hypochlorite after magnetic separation but prior to leaching (post-magnetic oxidation). It will be evident from this Table that with comparable flow rates (in gallons/minute) through the magnetic separating apparatus, the pre-magnetic oxidation yields far improved results.

TABLE I  
Effect of Sodium Hypochlorite upon Brightness of a No. 2 Clay Fraction

Clay Treatment	Leached Brightness	Flow Rate (gpm)
Normal	89.9	15.6
Postmagnetic-oxidation	90.2	15.6
Premagnetic-oxidation	91.15	15.6

In Figure 2 a graph appears, setting forth the effects upon leached brightness, of adding various concentrations of the preferred oxidant, NaOCl. The basic sequence in obtaining the depicted data involved addition of NaOCl to a slurry having a 30% solids content, followed by magnetic separation and customary leaching (with  $ZnS_2O_8$  and alum). No added dispersants such as sodium hexametaphosphate or sodium metasilicate were used. In general it is seen that where the oxidant is thus used alone, between 1/2 and 4 pounds per ton of clay may be usefully employed, with approximately 2 pounds/ton being a preferred optimal figure.

Where NaOCl is used alone, the beneficial effects of treatment are seen from Figure 2 to start to fall rather rapidly beyond the peak value of the curve, as concentration of NaOCl is increased. The basic problem here is that the NaOCl as the higher concentrations are reached, begins to increase the viscosity of the aqueous system the phenomenon being reminiscent of reflocculation. On consequence, even though the releasant effects may be augmented, the higher viscosities limit the effectiveness of magnetic separation by reducing the ability of the released contaminants to respond to the magnetic field. The effects of NaOCl on viscosity, are furthermore markedly dependent upon the solids content of the slurry treated. This

aspect of the invention is illustrated in the graph of Figure 3, wherein slurry viscosity is plotted as a function of percentage solids for a No 2 clay fraction. The curve C is a control curve, while the curve A illustrates the effects of adding 2 lbs/ton of NaOCl to the various solid content slurries. It is seen from this curve that the viscosity of the slurries rises very rapidly above a solids content of about 30 to 35%. From this it will be clear that treatment with NaOCl alone is preferably limited to slurries having solids content up to about 30 to 35%.

From the foregoing, the important advantage of incorporating dispersants such as the sodium hexametaphosphate mentioned (Calgon\*) will be appreciated. Referring this to Figure 4 a graph is set forth which is generally similar to Figure 2. The curve D is therefore seen to depict the effects upon brightness of No. 2 clay samples, of NaOCl concentrations. Curve E, in contrast, shows the resultant clay brightness achieved where 2 lbs/ton of Calgon\* are added. As was mentioned in connection with Figure 2 the data set forth are for a slurry with 30% solids content. It is seen here that the addition of the dispersant extends considerably the useful concentration range of the NaOCl. The Calgon\*, in particular, acts upon the clay component so as to lower the otherwise rising viscosity of the system. This result is illustrated in the following Table 2:

TABLE 2

NaOCl #/ton	Unleached Clay Brookfield Viscosity (cps)	Brookfield Vis- cosity/Calgon Add.
0	10	—
1	12	—
2	15	—
4	146	10
(#=lbs)		

The data in Table 2 are for a No. 2 fraction clay slurry with 30.7% solids. The data indicated for Calgon\* are for addition of 1#/ton to the slurry after NaOCl addition, and it is noted the additive lowers the viscosity to 10 cps in the presence of 4#/ton NaOCl level. Referring back to Figure 3, the important consequence is seen (from curve B therein) that where even 1#/ton of the Calgon\* is

added to the NaOCl-containing slurry, the viscosity remains relative flat up to quite high solids levels. In point of fact it is found that addition of 1 to 2 pounds per ton clay of the sodium hexametaphosphate (Calgon) can reduce the viscosity problem associated with use of NaOCl alone, as to allow effective magnetic separation at solids up to 50 to 55%, which is comparable to results possible with a deflocculated clay slurry.

With the addition of the specified small quantities of Calgon\*, up to about 8#/ton of NaOCl may be beneficially employed.

As also indicated in connection with Example I, one may consider the advantages yielded by the present invention to be of primary interest in that one may by employing the invention so increase the production rate capabilities of the magnetic separating processes so as to achieve a desired leached brightness level for comparatively much higher flow rates in the apparatus than would be possible in the absence of treatment by methods of the invention. Thus, in Table 3 hereinbelow, data are set forth indicating the rates at which a No. 2 fraction clay may be processed in identical magnetic separating apparatus to yield a 90 TAPPI brightness level. The Table 3 again compares a so-called "normal" magnetic separation treatment with treatments wherein post-magnetic oxidation (as a control) and pre-magnetic oxidation in accordance with the

principles of the invention are utilized. It is seen from Table 3 that, particularly where pre-magnetic oxidation is employed, much higher flow rates are possible and still yield the same leached brightness level. The Figures represented in Table 3 are processed average values; actual test data from which such tubular data were obtained are plotted in Figure 5. The data are taken upon a slurry having approximately 30% solids, with the NaOCl being added in concentrations of 2#/ton. It may be appreciated that the production rates, as shown in Table 3, are somewhat misleading in that they are strongly influenced by the indirect effect of flow rate upon slurry solids. However, the observed increase in flow rate (at a 90 brightness level) with oxidation treatment of the clay is the more direct confirmation of the beneficial effects of treatment with the oxidants in accordance with the invention.

TABLE 3  
Effect of Sodium Hypochlorite Upon the Rate of Production of No. 2 Fraction Clay

Clay Treatment	Flow Rate U.S. gallons/minute (gpm)	Production Rate tons/hour (tph)	Leached Brightness
Normal	13.4	0.23	90
Postmagnetic-oxidation	21.2	0.54	90
Premagnetic-oxidation	41.4	1.63	90

It is important in the foregoing connection to point out that some clays which are not readily susceptible to brightness improvements by the methods of the invention, yet are found to be markedly responsive to increased production rate. This is to say that by employing the invention the flow rates necessary to achieve a given brightness level, may in many cases be increased (i.e. retention time in the magnetic separator decreased), even though the absolute brightness level is but slightly raised. It has been shown in U.S. Patent 3,985,646, that brightness in the type of separation apparatus utilized with the present processes, saturates with increased efficiency of magnetic separation (increased field strength, retention time and packing density of the separation matrix). Hence if one is working with a well tuned separator, then any improvements in clay preparation which will allow for easier discolorant removal, will have a greater effect upon additional increase in production rate than upon brightness improvement. A number of clays have thus been observed which show marginal or modest brightness improvements where the present pre-magnetic separation treatments are used, but virtually all clays are investigated show pronounced reduction in

retention time for a specified brightness level. This, of course, implies increased production rate, as the latter is inversely related to retention time.

#### WHAT WE CLAIM IS:—

1. A method for removing discolorants from a clay comprising the steps of adding an oxidant to an aqueous slurry of a clay having weakly magnetically susceptible contaminant particles in minor concentration bound to the surface of the clay, so as to release chemically said particles from the clay surface, and magnetically separating the thus released particles from the clay.
2. A method as claimed in Claim 1, wherein said oxidant comprises sodium hypochlorite.
3. A method as claimed in Claim 2, wherein said hypochlorite is added in an amount of from 1/2 to 4 pounds/ton of clay.
4. A method as claimed in Claim 2, wherein said hypochlorite is added in quantities of up to 2 pounds/ton of clay.
5. A method as claimed in Claim 2, wherein said hypochlorite is added in an amount of from 1/2 to 8 pounds/ton of clay in said slurry, and further including the step of adding to the aqueous slurry one or more

dispersing agents to reduce the viscosity of said aqueous slurry.

- 5 6. A method in accordance with Claim 5, wherein said dispersing agent(s) is or are sodium metasilicate and/or sodium hexametaphosphate.

- 10 7. A method as claimed in Claim 6, wherein up to 2 pounds per ton clay of said sodium hexametaphosphate, and between 4 and 15 pounds per ton clay of said sodium metasilicate in the anhydrous form are added to the slurry and the pH in said slurry is maintained in the range of from 7 to 12.

- 15 8. A method as claimed in Claim 6, wherein said dispersing agent(s) is or are

added in concentration(s) maintaining the viscosity of said slurry below 15 centipoise.

9. A method as claimed in Claim 7, wherein said dispersing agent is sodium hexametaphosphate in a concentration of from 1 to 2 pounds per ton of clay. 20

10. A method as claimed in Claim 9, wherein said slurry contains up to 55% solids.

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FIG. 1

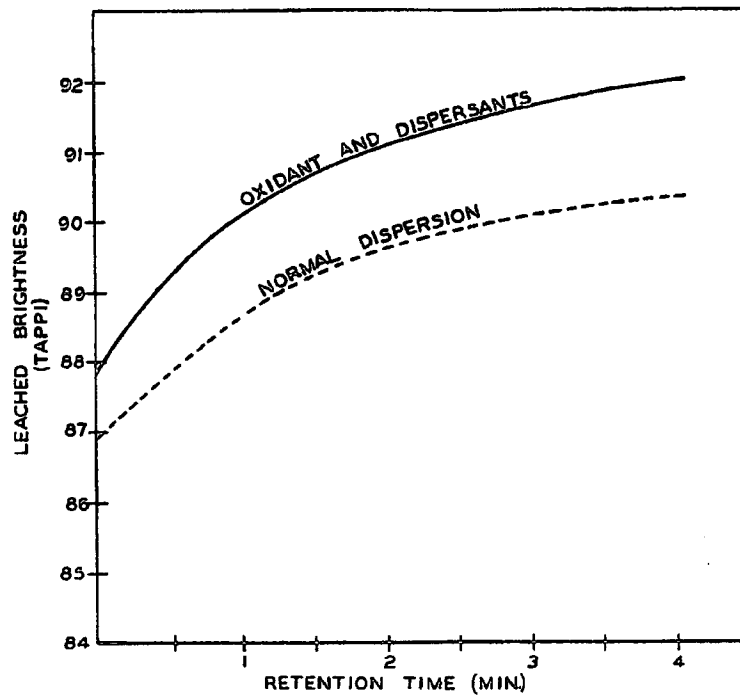
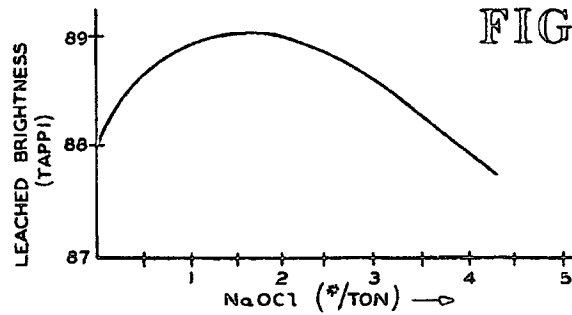


FIG. 2





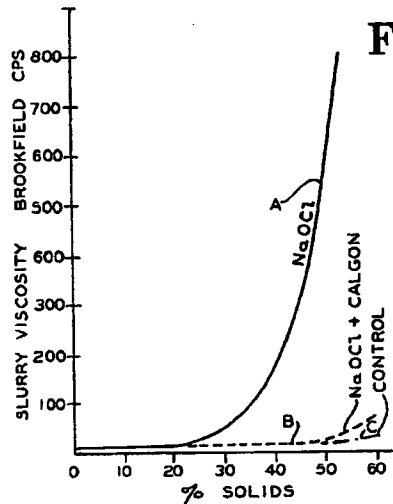


FIG. 3

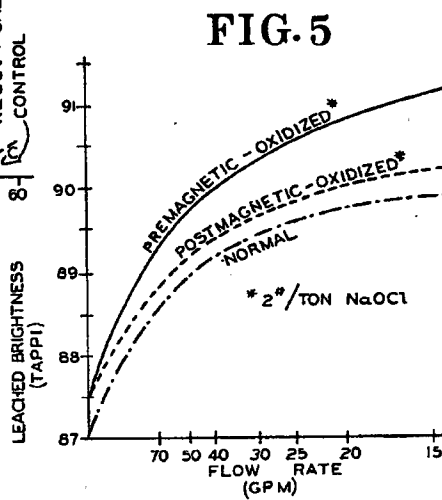


FIG. 5

FIG. 4

